Available online at www.sciencedirect.com

ScienceDirect

Procedia Earth and Planetary Science 10 (2014) 266 – 270

Procedia
Earth and Planetary Science

Geochemistry of the Earth's Surface meeting, GES-10

Rock-derived micronutrient transport in the Tropics: Molybdenum cycling in deeply-weathered Panama soils

Christopher B. Gardner[a], W. Berry Lyons[a], Guy Litt[b], Fred L. Ogden[b]

[a] *School of Earth Sciences, The Ohio State University, Columbus, OH 43210, USA*
[b] *Department of Civil and Architectural Engineering, University of Wyoming, Laramie, WY 82071, USA*

Abstract

The rock-derived micronutrient Molybdenum (Mo) is important in both terrestrial and ocean ecosystems as an essential cofactor in nitrogenase, the enzyme used by microorganisms to fix atmospheric nitrogen. As global nitrogen fixation rates respond to increasing atmospheric pCO_2, the weathering, transport, and availability of this micronutrient becomes essential, because Mo limitation on nitrogen fixation has been documented in diverse ecosystems, including tropical soils in Panama. Therefore, a thorough understanding of the carbon and nitrogen cycles may depend more on the availability of trace metals such as Mo than previously realized, but the weathering and cycling of these elements as they pass across ecosystem boundaries remains poorly understood. This work explores the sources and sinks of Mo in small (36-176 ha) single land cover catchments in tropical Panama. Water samples were collected from precipitation, canopy throughfall, soil water, groundwater, soil seeps, and first-order through higher-order streams. Though Mo is considered a "rock-derived" micronutrient, concentrations were higher in precipitation and shallow soil water than in the groundwater and stream waters in contact with underlying rocks and weathered saprolite. Event-based mass balance suggests that Mo is being retained within the catchment ecosystem. The source of Mo in tropical forests may have important implications as the amount of nitrogen fixation changes during tropical forest recovery from a previous land use.

Peer-review under responsibility of the Scientific Committee of GES-10

Keywords: Molybdenum, Panama, river chemistry, micronutrient

1. Introduction

The potential for atmospheric carbon sequestration by terrestrial vegetation and aquatic biota depends on interactions between the carbon cycle and other biogeochemical cycles that remain poorly understood. The nitrogen cycle is particularly important because it often limits the productivity of terrestrial ecosystems[1], and therefore carbon

Peer-review under responsibility of the Scientific Committee of GES-10
doi:10.1016/j.proeps.2014.08.057

storage. Nitrogen fixation is the primary nitrogen input to terrestrial ecosystems[2], and climate models containing a coupled carbon-nitrogen component suggest that global climate models without nutrient limitation may overestimate terrestrial carbon uptake and therefore underestimate future warming[1,3].

An additional layer of complexity controlling nitrogen dynamics is the cycling and availability of rock-derived micronutrients, principally iron (Fe) and molybdenum (Mo), that are essential for nitrogen-fixating organisms. The coupling of major nutrient cycles with these trace element cycles through basic stoichiometry, redox reactions, metabolic activity, and chelation are collectively referred to as "coupled biogeochemical cycles"[4]. The interactions among the carbon, nitrogen, and phosphorous cycles have been well studied, but the importance of the coupling between these cycles and trace element micronutrients are not nearly so well understood[5,6]. While many studies have focused on the response of nitrogen fixation to trace metal fertilization[7], we know much less about the production of soluble species through weathering, and transport of trace elements such as Mo across ecosystem boundaries, and the temporal scales over which these processes occur[6]. Because the availability of Mo is essential to nitrogen-fixing organisms[8], the unknown roles of coupled biogeochemical cycles involving Mo and their relationship with the carbon and nitrogen cycles, represent a major source of uncertainty in modeling and predicting future climate change.

Recent work by Wichard et al. (2009)[9] described local Mo cycling in terrestrial forests, showing that leaf litter binds Mo in shallow soils, providing Mo to N-fixing bacteria, which in turn provide trees with bioavailable N in a mutualistic relationship. This suggests that the interruption of this cycle by changing landuse away from forested ecosystems may have a significant effect on Mo cycling. Recent work in the Agua Salud experimental catchment in Panama shows that nitrogen fixing trees are able to relieve N limitation in recovering tropical forests and provide a large fraction of the N needed support forest growth and C sequestration in biomass[10]. Fixation increases during the transition from an agricultural land use and though growth phases, and then decreases as the forest matures. Given the deeply weathered Mo-deficient soils in the region, what is the source of Mo for nitrogen fixers in this recovering ecosystem? This is especially important because Mo limitation on nitrogen fixation has been documented in tropical soils in Panama[7].

2. Study Area and Methods

The Agua Salud Project has been managed by the Smithsonian Tropical Research Institute since 2008 to study the impact of landuse change on ecosystem services within the Panama Canal watershed. Soils within the Agua Salud Project sites are deeply weathered oxisols typical of tropical regions worldwide. These oxisols are derived from in-situ weathering of the underlying basaltic lithology, which outcrops in the deeply-incised stream channels. We examined three catchments within the 650ha research site. The forested catchment (142ha) is located entirely within Soberanía National Park, and is dominated by old mature forest (>80 years old) and approximately 20% younger secondary forest (<34 years old)[11]. The mosaic catchment (176ha) contains a mix of young secondary forest (<15 years old), actively grazed cattle pasture, and a small amount of subsistence farming. The pasture catchment (36ha) is the actively grazed cattle pasture sub-basin located within the mosaic catchment. The mosaic and forest catchments contain clustered tipping bucket rain gauges, and all catchments' outlet streams are equipped with a V-notch weir, pressure transducer, and a model 6712 ISCO automated water sampler with a 730 bubbler module.

Precipitation, canopy throughfall, groundwater, soil pore waters (10, 50 and 100cm depths), and stream baseflow samples were collected from the Agua Salud Project catchments during May-June, 2013, at the onset of the wet season in Panama. The automated stream samplers also collected event-based stream samples at regular intervals during the rising and falling limbs of the hydrograph during several rain events. Samples were filtered in the field using polypropylene syringes and 0.45µm syringe filters into acid cleaned LDPE bottles. Major ions were analyzed using a Dionex DX-120 Ion Chromatograph, and trace elements were analyzed using a Thermo Scientific Element2 High Resolution ICP-MS.

3. Results and Discussion

Molybdenum concentrations generally decrease from "top to bottom" in these catchments (Figure 1). Mean Mo concentrations in precipitation were 500pM (n=6), which were equivalent to shallow soil water concentrations, also

approximately 500pM (n=17). These concentrations in precipitation are consistent with literature values of 20-1300pM[12]. Canopy throughfall concentrations were highly variable and dependent on the flushing of dry deposition off of the canopy. Mean Mo concentrations in groundwater were 270pM, and mean concentrations in the streams were 240pM (forest catchment), 250pM (mosaic catchment), and 170pM (pasture catchment). Though Mo is generally thought of as a "rock-derived" micronutrient, the primary source of Mo to the waters in these catchments appears to be precipitation.

Molybdenum is primarily present as molybdate (MoO_4^{-2}) in bulk precipitation, though a fraction is also associated with particulate matter (e.g. Fe(III)-hydroxides) in initial rainout[13]. It is the highest concentration transition metal in the ocean (104 nmol kg^{-1} as MoO_4^{-2})[12], and given the close proximity of the study site to both the Atlantic and Pacific oceans, cyclic sea salt is a possible source of Mo in local precipitation. However, the Mo:Cl ratio in seawater ($0.2 \cdot 10^{-6}$) is more than two orders of magnitude lower than waters in the Agua Salud (precipitation=$66 \cdot 10^{-6}$, throughfall=$17 \cdot 10^{-6}$, soil water=$6 \cdot 10^{-6}$, groundwater=$2 \cdot 10^{-6}$, stream water=$2 \cdot 10^{-6}$). Molybdenum is also associated with dust and airborne particulates from fossil fuel combustion[13], and given the Mo:Cl ratios observed, one or both of these sources must be invoked.

In the earth's crust, Mo is associated with sulfide minerals, and the Mo present in stream waters is primarily the result of pyrite weathering[12]. However, groundwater, soil water, and stream waters within the Agua Salud Project sites show no correlation with sulfate concentrations, suggesting pyrite as an unlikely source. Additionally, Mo concentrations in the Agua Salud Project streams are very low compared to global rivers, and fall within the low to medium range of published precipitation values[12].

A Mo mass balance was calculated for several events. The Mo influx via precipitation used a constant mean of 500pM Mo concentration and precipitation over the catchment measured by rain gauges. Mo outflux was determined from samples collected by automated ISCO samplers in conjunction with weir flow data. The simple mass balance approach suggests that Mo is being retained within the catchments. For example, during a June 15th precipitation event on the pasture catchment, a total of 104mm of rain fell on the catchment (37,500m^3), containing ~19 millimoles of Mo. This event produced 22,500m^3 of runoff containing ~1.5 millimoles of Mo. This simple model results in 87% Mo storage within the catchment during the event.

After Mo enters the catchment as soluble molybdate through precipitation, there are several ways it may be retained within the critical zone. Recent work has shown that nearly all Mo present on the soil surface is bound with organic matter in leaf litter where it can then be taken up by diazotrophs for nitrogen fixation or plants for nitrate reductase used in nitrogen assimilation[9]. Molybdenum concentrations typically decrease down the soil profile where it is increasingly adsorbed onto Fe(III)-hydroxide mineral surfaces at less than neutral pH[14]. However, association with organic matter, particularly tannins, at the soil surface tends to keep Mo from leaching down further in the soil profile[9]. It is unknown which of these processes is dominant in the Agua Salud project catchments where subsurface hydrologic flow is heavily controlled by soil pipes, shallow macropores, and other preferential flowpaths[11], but soil water concentrations suggest Mo is retained in the shallow soil (Figure 1). The model is currently being refined with hydrograph separation techniques using δD/δ18O and Ge/Si ratios to better understand the relative contributions of new event water and baseflow.

Molybdenum weathering and cycling in the terrestrial environment remains poorly understood. This work suggests that in highly weathered tropical soils where weatherable Mo is scarce, precipitation may be an important source of Mo. Mass balance calculations suggest that precipitation-derived Mo is retained in the shallow soil where it may be available to nitrogen fixing organisms and plants.

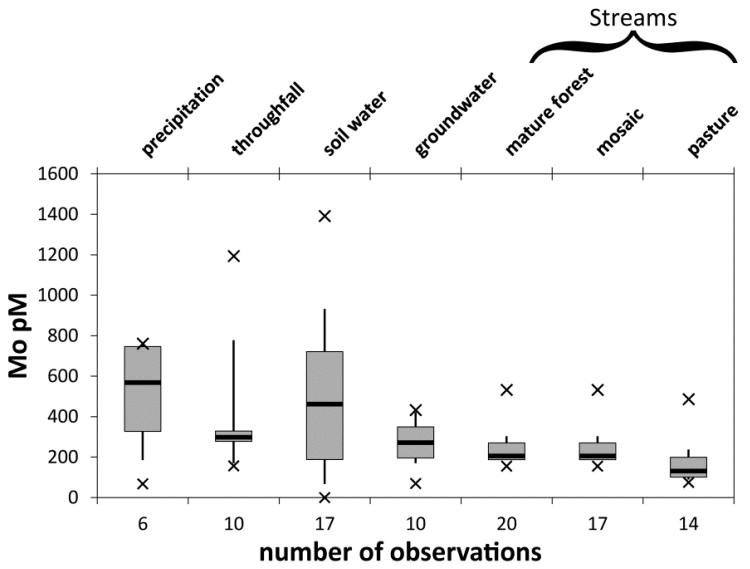

Figure 1. Box plot of molybdenum concentrations in the Agua Salud catchments. The gray box represents the 25th – 75th percentile, the black line denotes the median, the bars represent the 10th and 90th percentiles, and the Xs represent the maximum and minimum values.

Acknowledgements

This work was made possible by National Science Foundation Division of Earth Sciences grant #1045166 and the National Science Foundation Graduate Research Fellowship under grant #1001527A. We would like to thank Jefferson Hall and the Smithsonian Tropical Research Institute, Anthony Lutton and John Olesik at the Trace Element Research Lab at The Ohio State University.

References

1. Wang, Y-P, & Houlton, BZ. Nitrogen constraints on terrestrial carbon uptake: Implications for the global carbon-climate feedback. *Geophys Res Lett* 2009; **36**: L24403.
2. Galloway, J, Dentener, F, Capone, D, Boyer, E. Nitrogen cycles: past, present, and future. *Biogeochemistry* 2004; **70:**153–226.
3. Thornton, PE, Lamarque, J-F, Rosenbloom, N A, Mahowald, NM. Influence of carbon-nitrogen cycle coupling on land model response to CO_2 fertilization and climate variability. *Global Biogeochem Cy*, 2007; **21**:1–15.
4. Schlesinger, WH, Cole, JJ, Finzi, AC, Holland, EA. Introduction to coupled biogeochemical cycles. *Front Ecol Environ* 2011; **9**:5–8.
5. Burgin, AJ, Yang, WH, Hamilton, SK, Silver, WL.Beyond carbon and nitrogen: how the microbial energy economy couples elemental cycles in diverse ecosystems. *Front Ecol Environ* 2011; **9**: 44–52.
6. Finzi, AC, Cole, JJ, Doney, SC, Holland, EA, Jackson, RB. Research frontiers in the analysis of coupled biogeochemical cycles. *Front Ecol Environ.* 2011; **9**(1): 74–80.
7. Barron, AR, Wurzburger, N, Bellenger, JP, Wright, SJ, Kraepiel, AML, Hedin, LO. Molybdenum limitation of asymbiotic nitrogen fixation in tropical forest soils *Nat Geosci.* 2009; **2**: 42–45.
8. Bellenger, JP, Wichard, T, Kustka, AB, Kraepiel, AML. Uptake of molybdenum and vanadium by a nitrogen-fixing soil bacterium using siderophores *Nat Geosci.* 2008; **1**: 243–246.
9. Wichard, T, Mishra, B, Myneni, SCB, Bellenger, J-P, Kraepiel, AML.Storage and bioavailability of molybdenum in soils increased by organic matter complexation. *Nat Geosci.* 2009; **2**: 625–629.
10. Batterman, SA, Hedin, LO, van Breugel, M, Ransijn, J, Craven, DJ, Hall, JS. Key role of symbiotic dinitrogen fixation in tropical forest secondary succession. *Nature* 2013; **502**: 224–227.

11. Ogden, FL, Crouch, TD, Stallard, RF, Hall, JS. Effect of land cover and use on dry season river runoff, runoff efficiency, and peak storm runoff in the seasonal tropics of Central Panama. *Water Resour Res* 2013; **49**, 1-20.
12. Miller, CA, Peucker-Ehrenbrink, B, Walker, BD, Marcantonio, F. Re-assessing the surface cycling of molybdenum and rhenium. *Geochim Cosmochim Ac* 2011; **75:** 7146–7179.
13. Kawakubo, S, Hashi, S, Iwatsuki, M. Physicochemical speciation of molybdenum in rain water. *Water Res* 2001; **35:** 2489–2495.
14. Gustafsson, J P. Modelling molybdate and tungstate adsorption to ferrihydrite. *Chem Geol* 2003; **200:** 105–115.